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Research Article

Determination of Pesticide Residues in Surface and Ground Water from Wurno Irrigation Farms and Environs in Sokoto State, Nigeria

[1]Osesua, B.A.,[2]Tsafe, A.I.,[2]Birnin-Yauri, U.A. and [3]Sahabi, D.M.
[1]Science Lab. Tech. Waziri Umaru Federal Poly. Birnin Kebbi, Kebbi State, Nigeria
[2]Dept. of Pure and Applied Chemistry. UDUS., Sokoto, Nigeria.
[3]Dept. of Biochemistry. UDUS., Nigeria.
Correspondence: osesuaa@yahoo.com

Abstract

The organochlorines (OCs) and organophosphorus (OPs) pesticides in water from Wurno irrigation farm having intensive agricultural activities were investigated to evaluate their levels of pollution in the environment. Sampling was done using grab method. Samples were subjected to Liquid-liquid extraction using ethylacetate /dichloromethane mixture (1:1) and clean-up on silica gel adsorbents. The detection and determination of the pesticide residues were performed using Gas-Chromatographic technique (GC-MS) coupled with MSD. The results obtained revealed that DDD one of the metabolites of DDT showed the highest mean concentration levels of 1.002µg/L with a percentage distribution of 27.32%. The next most abundant detectable residues was DDE detected in fifteen samples with a mean concentration of 0.927µg/L and a percentage distribution of 25.41% γ-HCH was detected in eighteen samples with a mean concentration of 0.896µg/L and a percentage distribution of 24.59%. DDT has a mean concentration of 0.894µg/L and a percentage distribution of 24.32%. Among the organophosphorus, chlorpyriphos showed the highest mean concentration of 1.073µg/L measuring a total of 69.05% of the detectable residues. Methylparathion was the next abundant organophosphorus with a mean concentration of 0.162µg/L and a percentage distribution of 10.32%. Among the residues, water samples were found to be more contaminated by organochlorine pesticide residues than the organophosphorus residues. Generally the mean concentration levels of individual pesticide detected in the samples are higher than the WHO maximum limits indicating a possible pollution of the water environment by the agricultural activities.

Key words: organochlorine organophosphorus, endosulfan, endrin, DDT, HCH.

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Introduction

Organic contaminants present in the environment are a result of different sources of pollution from anthropogenic activities (Reemtsma and Jekel, 2006). The pesticides, generated by the intensification of agriculture, are regarded as some of the most dangerous contaminants of the environment, despite their numerous merits. Not only are they toxic; they are also mobile and capable of bioaccumulation. On top of this, they can take part in various physical, chemical and biological processes. Many of these pesticides are characterized by a strong persistence which explains their wide presence in the different compartments of the environment (Barth *et al.*, 2007). Due to these physicochemical characteristics and their extensive use, many of these pesticides end-up in surface and ground water. They are found nowadays in all surface waters and in a growing number of aquifers. Their presence in water is considered as a potential risk not only for drinking water quality and human health, but also for ecosystems (Bailey *et al.*, 2012).

Worldwide pesticide usage has increased dramatically during the last three decades coinciding with changes in farming practices and the increasing intensive agriculture. This widespread use of pesticides for agricultural and nonagricultural purposes has resulted in the presence of their residues in various environmental matrices. Numerous studies have highlighted the occurrence and transport of pesticides and their metabolites in rivers (Konstantinou *et al.,* 2006), channels (Miiller, 2000), lakes (Hela,2005; Kannan *et al.,* 2005), sea (Albaiges, 2005; Sapozhnikova *et al*., 2004), air (Harrie, 1999; Tuduri, 2006), soils (Sanchez-Bronete *et al.,* 2004; Goncalves, 2006), groundwater (Guzzella *et al.,* 2006; Sahoo, 2006), and even drinking water (Bartram, 2002; Maloschik, 2007), proving the high risk of these chemicals to human health and environment.

In recent years, the growing awareness of the risks related to the intensive use of pesticides has led to a more critical attitude by the society toward the use of agrochemicals. At the same time, many national environmental agencies have been involved in the development of regulations to eliminate or severely restrict the use and production of a number of pesticides (Directive 91=414=EEC) (EEC, 1991). Despite these actions, pesticides continue to be present causing adverse effects on human and the environment. Monitoring of pesticides in different environmental compartments has been proved a useful tool to quantify the amount of pesticides entering the environment and to monitor ambient levels for trends and potential problems and different countries

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have undertaken, or currently undertaking, campaigns with various degrees of intensity and success (Wiersma, 2004).

The widespread use of pesticides for agricultural and nonagricultural purposes has resulted in the presence of their residues in surface and ground water resources. The physicochemical properties of pesticide compounds, particularly their solubility in water and organic solvents, characterized by their octanol-water partition coefficients, determine their character of leaching into surface and ground waters (MacBean, 2015). Depending on their chemical stability, these substances may undergo decomposition processes; therefore, not only active ingredients but their metabolites may also occur as contaminants (Aizawa, 1989). Most pesticides released into the environment are regarded as toxic substances, and newly emerging toxicological interactions have also been identified (mutagenicity, carcinogenicity, hormone modulant effects of environmental Endocrine Disruptor Chemicals (EDCs), immunomodulant effects). Unfortunately not only pesticide residues but also other organic micropollutants (pharmaceuticals, personal care products, etc.) deteriorate water quality. Surfactants are common additives in agrochemical formulations to improve water solubility and uptake of the active ingredient and enhance its pesticide efficacy. Residues of surfactants are often detected in the environment; thus they can influence the effect of pesticide active ingredients. Recent studies indicate that combined toxicity of pesticide residues with other chemicals in agricultural use (e.g., adjuvants, detergents) has to be considered (Krieger, 2010).

Contamination occurs not only due to current use of agrochemicals but also due to leaching of persistent ingredients from soil. Pesticide contamination of surface water in a particular region depends on several factors, such as closeness of crop fields to surface water, characteristics of surrounding fields (soil, grassland, slope, and distance to water bodies), and climate conditions (temperature, humidity, wind, and precipitation). In consequence, pesticide residues are being reported as common organic contaminants worldwide in surface waters and other environmental matrices (Gilliom *et al*. 2007; Rathore and Nollet, 2012; Ali *et al*. 2014).

If the credits of pesticides include enhanced economic potential in terms of increased production of food and fiber, and amelioration of vector-borne diseases, then their debits have resulted in serious health implications to man and his environment. There is now overwhelming evidence that some of these chemicals do pose potential risk to humans and other life forms and unwanted side effects to the environment (Forget, 1993; Igbedioh, 1991). Ideally a pesticide must be lethal to the targeted pests, but not to non-

target species, including man. Unfortunately, this is not so. The controversy of use and abuse of pesticides has surfaced. The rampant use of these chemicals, under the adage, "if little is good, a lot more will be better" has played havoc with human and other life forms (Karunakarani, 2008).

The contamination of water bodies is a major source of concern since it is the habitat for fish and other aquatic organisms which are major sources of protein for most people in the region. An uncontrolled chemical activity in water bodies implies a high rate of exposure to humans who obtain much of their protein nutrition from these sources, and also to those who take in vegetable produced using such waters as means of irrigation. On the other hand, some amount of the chemicals used in the form of pesticides end up in the tissue of aquatic organisms and bio-accumulates with time (Jires *et al*. 2002).

The presence of pesticides in water (particularly bio-refactory organics that is aromatic chlorinated hydrocarbons) impacts objectionable and offensive taste, odours and colours to fish and aquatic plants even when they are present in low concentrations (De, 2003).

The organochlorine (OC) pesticides are among the major types of pesticides, notorious for their high toxicity, their persistence in the physical environment and their ability to enter the food chain (Jiries *et al*. 2002). Although the production and use of many types of OCs and organophosphorus (OPs) have been severely limited in many countries including Nigeria, they are, nevertheless, still being used unofficially in large quantities in many parts of Nigeria, and in other developing countries because of their effectiveness as pesticides and their relatively low cost (Ntow, 2001: Ntow, *et al*. 2006).

The OCs, unlike the OPs pesticides are much more resistant to microbial degradation and have a propensity to concentrate in lipid rich tissues of aquatic organisms and most mammals. These properties lead directly to their most undesirable characteristics – the environmental persistence, bio-concentration, and bio-magnification through the food chain. Unlike the OPs – dichlorvos, diazinon, chlorpyriphos and fenitrothion – which are readily deactivated and degraded by micro-organisms and therefore do not readily accumulate, the OCs residues are detectable in most surface water bodies and are bioconcentrated in shellfish and other biota in these ecosystems (Holland *et al*. 1995).

The aim of this work is to determine the concentration of organophosphorus (OP) and organochlorine (OC) pesticide residues from water collected from Wurno irrigation farm

and environs where these chemicals have been used extensively to improve agricultural crop production.

Materials and Methods

Description of Sample Site

The study area was in Wurno Irrigation farm located in Wurno Local Government Area of Sokoto State. The total farm areas cover over 1200 hectre. The area is densely populated, rich in agriculture and a major producer of rice, millet, maize, onions and vegetables, etc. for the state and neigbouring country. Cattle, sheep, goat, and poultry are also kept. The area is popularly known for the extensive dry season farming which is facilitated by the establishment of a dam. The sampling sites for residue determination were specifically located in the farm irrigation area, where pesticides are extensively used to control weeds and other pests. Samples were also collected from the Lugu and Rima River which flow directly into the dam (Fig. 1).

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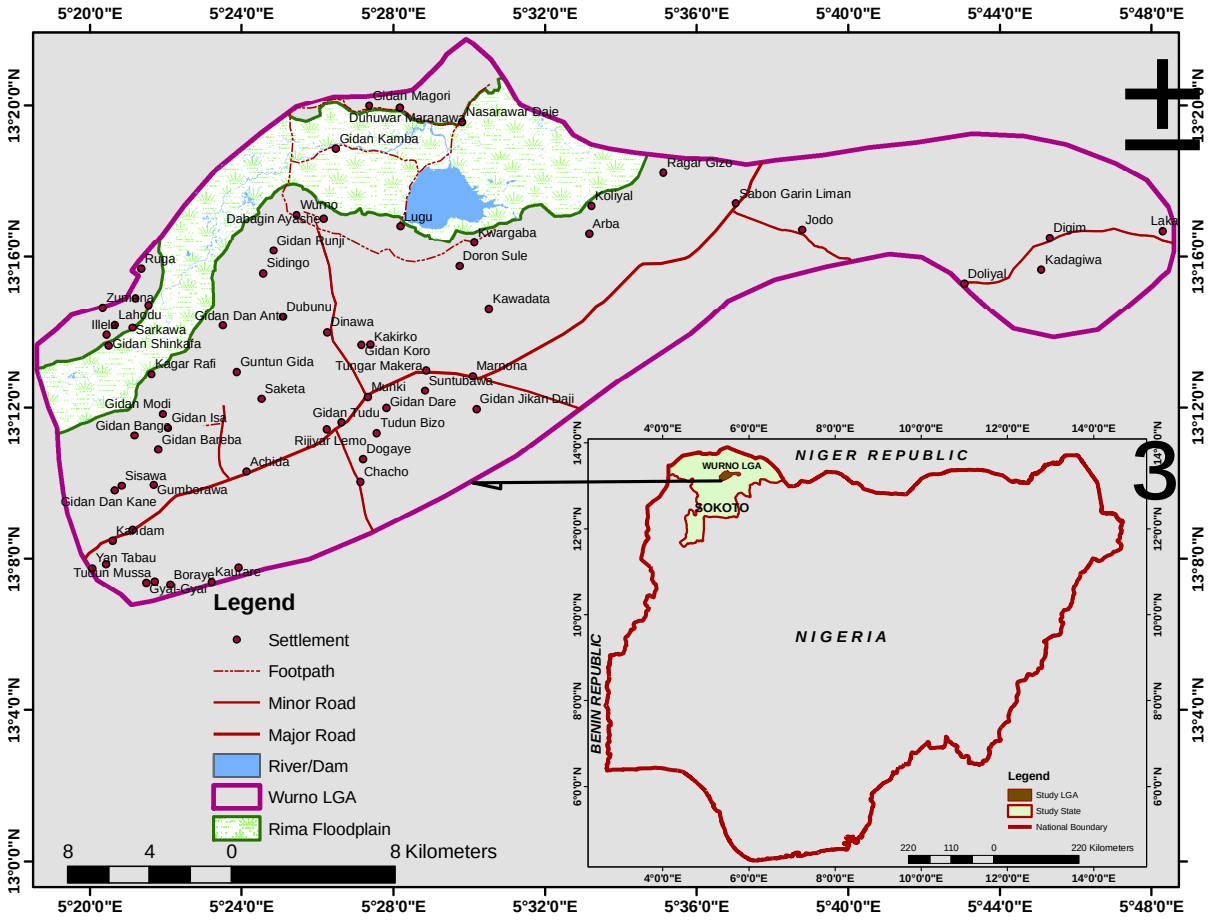

Fig. 1: Map of Nigeria showing the location of Wurno Local Government Area and the sampled area.

Sampling Method

The method employed by EPA as reported by (Gregg, 2009) was adopted for the collection of water samples. Four (4) water samples on the river path were collected at different site at an average interval of 400m – 500m. Each sample is a composite of three sub-samples. These were homogenized and labeled (RWS). Another Five (5) water samples were collected from irrigation tube well with an average depth of 12 – 20m. The distance between any two tube wells chosen for study was at least 0.2 km. The composite samples were homogenized and labeled (TWS). Five (5) samples were also collected from hand dug well within the irrigation farm, with an average distance as above,

homogenized and labeled as (HWS). Fresh water (3 samples) from the dam was also collected with an average distance of 250m between each sample and the samples homogenized and labeled (FWS). Finally, three (3) bored-hole water (ground water) samples within the town was collected and labeled (BWS).

Total numbers of twenty (20) water samples were collected from different sites. Grab sampling method was used. Samples were collected in 2.5 liter amber colored glass bottles. Sampling bottles were rinsed well with distilled water and n-hexane, and then air dried, and was carefully filled to overflowing, without trapping air bubbles in sealed bottles. The samples were transported in cool-box with ice packs to the laboratory prior to analysis.

All composite samples collected in prerinsed screw cap glass water bottles taken to the laboratory, were stored between 4^0C – 8^0C prior to analysis.

Extraction of Pesticides Residues From The Samples

The extraction technique employed in this work was the US EPA Method 3510 (US-EPA, 2004) for aqueous matrix for the analysis of semi-volatile and non-volatile organics. The extracts were cleaned up by using the US EPA Method 3620B (US-EPA, 2009).

Exactly 500 mL of the aqueous sample was measured and transferred into a 1000 mL separatory funnel. The aqueous sample was extracted three times with portions 100 mL of 1:1 (v/v) ethyl acetate/dichloromethane mixture. The separatory funnel was shaken for 2-3minutes, letting out the pressure intermittently and clapped for 30 min to allow phase separation. The combined organic phases were collected into a 500 mL beaker with the aqueous phase discarded. The combined organic layer was then dried of any aqueous substance with 20 g of anhydrous sodium sulfate and allowed to settle. The organic content was then decanted into a 250 mL round bottom flask and the content evaporated to dryness using the rotary evaporator at 40°C. The pesticide in the rotary flask was then dissolved and collected with 2 mL of ethyl acetate and transferred into a 2 mL vial ready for a clean-up.

Clean-Up of Sample Extracts

Ten grams (10g) portion of deactivated silica gel was weighed and transferred into a 10 mm i.d. glass chromatographic column followed by the addition of 3g of anhydrous sodium sulfate. 10mL of the 1:1 (v/v) ethyl acetate/dichloromethane mixture was used to wet and rinse the column. The extract residue in 2 mL ethyl acetate was then

transferred into the column and the extract vial rinsed (three times) with 2 mL ethyl acetate and added to the column. The column was then eluted with 80 mL portion of ethyl acetate/dichloromethane at a rate of 5 mL/min into a conical flask as fraction one. The column was eluted again with 50 mL portion of ethyl acetate/dichloromethane for the second elution and added to the first extract (US-EPA, 2009).

All the fractions of each sample were concentrated to dryness using a rotary evaporator at 40°C. Each residue was then dissolved and collected in 2 mL ethyl acetate for GC-MS analysis.

Sample Analysis

GC-MS analysis was carried out on Agilent Technologies 6890N Network GC System and Agilent Technologies Network Mass Selective Detector couples with 7683B Series Injector. The model number of the column used was Agilent 122-5533 capillary column with specification: DB-5ms, 0.25mm*30m*1µm. The carrier gas used was helium at a flow rate of 1.2m/min. The injection volume was 1µmL. The inlet temperature was maintained at 230^{O}C. The oven temperature was programmed initially at 50^{O}C for 5 minutes, then programmed to increase to 300^{O}C at a rate of 10^{O}C ending with 25 minutes, this temperature was held for 15 minutes. Total run time was 45 minutes. The MS transfer line was maintained at a temperature of 250^{O}C. The source temperature was maintained at 230^{O}C and the MS Quad at 150^{O}C. The ionization mode used was electron ionization mode at 70eV. The Ion Count (TIC) was used to evaluate for compound identification and quantitation. The Spectrum of the separated compound was compared with the database of the spectrum of known compound saved in the NIST02 Reference Spectra Library. Data analysis and peak area measurement was carried out using Agilent Chemstation Software.

Method validity

The recovery analysis and the validation of the extraction method were carried out at a fortification level of 0.5 mg/kg by introducing 25 mL of a mixed standard pesticide solution containing 25 µg/L of dichlorodiphenyl dichloroethylene (2,4'-DDE), 4,4'-dichlorodiphenyldichloroethane (4,4'-DDD), p,p'-dichlorodiphenyltrichloroethane [p,p'-DDT(r)(i)(f)] 100 mL of distilled water was measured out into a 100 mL measuring cylinder and transferred into a 300 mL separatory funnel. 25 mL of a 2 mg/kg mix standard pesticide solution was introduced into the funnel containing the distilled water and then swirled gently. The pesticides in the water were then extracted with two portions of 100 mL of 1:1 (v/v) ethyl acetate/dichloromethane solution. The extract

obtained – placed in a 200 mL round bottom flask – was then cleaned using a silica gel clean-up and then reduced to near dryness using a rotary evaporator at 40 °C. Solvent exchanged was carried out by dissolving and collected the content with 2 mL of ethyl acetate and then transferred into a 2 mL vial for subsequent analysis.

The validation analysis gave an average of 75 % extraction efficiency and an average reproducibility of 93 % indicating that the analytical process was efficient.

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Results and Discussion

Table 1: Organochlorine Pesticide Residues in the Sample (Conc. µg/L)

Samples	γHCH	α-endosulfan	β-endosulfan	Heptachlor	DDT	DDD	DDE	Endrin	Dieldrin	Drins	Total
RWS1	0.020±0.001	ND	0.051±0.020	ND	0.052±0.010	0.070±0.010	0.090±0.041	ND	ND	ND	0.283
RWS2	0.030±0.002	0.010±0.010	0.020±0.002	ND	0.031±0.004	ND	ND	ND	ND	ND	0.091
RWS3	0.021±0.001	0.020±0.001	0.021±0.001	0.011±0.001	0.060±0.010	ND	ND	ND	ND	ND	0.133
RWS4	0.020±0.001	ND	ND	0.020±0.001	0.051±0.021	0.060±0.003	0.042±0.002	0.011±0.001	0.020±0.001	ND	0.224
TWS1	1.570±0.060	0.310±0.002	0.220±0.008	0.230±0.160	1.050±0.030	1.211±0.022	1.300±0.002	0.010±0.001	0.010±0.001	0.020±0.001	5.931
TWS2	1.210±0.090	0.250±0.061	0.250±0.210	0.211±0.003	1.100±0.007	1.090±0.050	1.120±0.010	0.030±0.001	0.030±0.001	0.051±0.001	5.341
TWS3	1.552±0.130	0.231±0.009	0.201±0.002	0.250±0.040	1.311±0.200	1.110±0.006	1.130±0.004	0.020±0.001	0.060±0.004	0.070±0.004	5.935
TWS4	1.310±0.112	0.270±0.020	0.270±0.040	0.301±0.005	1.510±0.120	1.250±0.020	1.121±0.020	0.010±0.001	ND	0.020±0.001	6.062
TWS5	1.750±0.008	0.330±0.110	0.260±0.005	0.370±0.009	1.340±0.100	1.332±0.007	1.251±0.051	0.011±0.007	ND	0.010±0.002	6.914
HWS1	1.661±0.120	0.910±0.101	0.890±0.110	0.590±0.006	1.520±0.161	1.560±0.002	1.490±0.004	0.020±0.001	ND	0.030±0.001	8.671
HWS2	1.810±0.009	0.770±0.050	0.791±0.003	0.770±0.060	1.211±0.080	1.320±0.110	1.450±0.120	ND	ND	0.051±0.001	8.172
HWS3	1.800±0.003	0.511±0.060	0.450±0.006	0.711±0.061	1.600±0.113	1.430±0.008	1.400±0.100	0.011±0.002	0.010±0.001	0.040±0.003	7.963
HWS4	1.620±0.110	0.580±0.041	0.472±0.020	0.630±0.030	1.630±0.120	1.671±0.120	1.681±0.063	ND	ND	0.031±0.005	8.315
HWS5	1.711±0.040	0.570±0.060	0.520±0.005	0.550±0.033	1.810±0.008	1.880±0.060	1.800±0.099	0.010±0.001	ND	0.010±0.001	8.861
FWS1	0.010±0.001	ND	ND	0.030±0.001	0.020±0.001	0.033±0.001	0.010±0.001	ND	ND	0.031±0.001	0.134
FWS2	ND	ND	ND	0.010±0.002	ND	ND	ND	ND	ND	0.010±0.007	0.020
FWS3	ND	ND	0.010±0.001	ND	ND	ND	ND	ND	ND	0.011±0.004	0.021
BWS1	0.010±0.005	ND	ND	0.011±0.002	0.020±0.009	0.021±0.001	0.010±0.001	0.012±0.001	ND	0.014±0.001	0.098
BWS2	0.012±0.001	0.014±0.001	ND	ND	ND	ND	0.011±0.008	ND	ND	ND	0.037
BWS3	0.010±0.001	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.010
Mean Value	0.896	0.367	0.316	0.313	0.894	1.002	0.927	0.015	0.026	0.028	3.661
No. of samples Pesticide was Identified.	18	13	14	15	16	14	15	10	05	14	20
Min residue.	0.010	0.010	0.010	0.010	0.020	0.021	0.010	0.010	0.010	0.010	0.010
Max. residue.	1.810	0.910	0.890	0.770	1.810	1.880	1.800	0.030	0.060	0.070	8.861
W.H.O, (2010)	0.01	0.01	0.01	0.03	0.02	0.01	0.01	0.02	0.01	0.02	0.05

NOTE: Mean ±SD of triplicate, ND = Not Detected.

Table 2: Organophosphorus Pesticide Residues in the Sample (Conc. µg/L)

Samples	Dimethoate	Mevinphos	M/Parathion	Chlorpyriphos	Dichlorvos	Profenofos	Marathion	Parathion	Total	TotalOC+OP
RWS1	ND	ND	0.050±0.002	0.150±0.011	ND	ND	0.010±0.001	0.020±0.001	0.230	0.513
RWS2	ND	ND	0.031±0.006	0.112±0.006	ND	ND	ND	ND	0.143	0.234
RWS3	0.010±0.001	ND	0.066±0.012	0.122±0.002	ND	ND	ND	ND	0.198	0.331
RWS4	0.020±0.004	ND	0.092±0.003	0.144±0.002	ND	ND	ND	0.011±0.007	0.267	0.491
TWS1	0.020±0.002	0.031±0.007	0.121±0.002	1.151±0.311	0.050±0.013	0.033±0.001	0.061±0.011	0.130±0.004	1.597	7.528
TWS2	0.061±0.011	0.052±0.001	0.160±0.006	1.322±0.011	0.110±0.005	0.055±0.016	0.092±0.003	0.171±0.004	2.023	7.364
TWS3	0.090±0.004	0.055±0.007	0.191±0.006	1.450±0.119	0.071±0.002	0.010±0.001	0.041±0.005	0.150±0.003	2.058	7.993
TWS4	0.050±0.003	0.091±0.010	0.207±0.001	1.490±0.004	0.022±0.007	0.020±0.001	0.055±0.002	0.114±0.002	2.049	8.111
TWS5	0.090±0.005	0.077±0.003	0.231±0.013	1.432±0.005	0.060±0.002	0.022±0.004	0.099±0.013	0.177±0.005	2.188	9.102
HWS1	0.101±0.002	0.093±0.003	0.181±0.009	1.246±0.020	0.121±0.007	0.052±0.002	0.108±0.066	0.133±0.011	2.035	10.706
HWS2	0.091±0.006	0.140±0.007	0.233±0.003	1.611±0.019	0.134±0.004	0.092±0.013	0.077±0.023	0.151±0.009	2.529	10.649
HWS3	0.122±0.003	0.122±0.002	0.266±0.005	1.670±0.060	0.113±0.006	0.033±0.001	0.091±0.004	0.122±0.071	2.539	10.502
HWS4	0.170±0.015	0.151±0.006	0.291±0.009	1.810±0.081	0.116±0.004	0.071±0.003	0.114±0.002	0.199±0.011	2.922	11.237
HWS5	0.190±0.008	0.124±0.011	0.277±0.003	1.870±0.044	0.126±0.011	0.092±0.004	0.121±0.011	0.176±0.008	2.976	11.837
FWS1	0.031±0.003	ND	ND	0.991±0.003	ND	ND	0.010±0.001	ND	1.032	1.166
FWS2	ND	ND	ND	0.911±0.212	ND	ND	0.011±0.004	ND	0.922	0.942
FWS3	ND	0.017±0.008	0.033±0.009	0.772±0.011	0.014±0.001	ND	ND	0.033±0.001	0.869	0.967
BWS1	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.098
BWS2	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.037
BWS3	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.010
Mean Value	0.080	0.086	0.162	1.073	0.085	0.048	0.067	0.122	1.563	5.224
No. of Samples Pesticide was Identified	13	11	15	17	11	10	13	13	17	20
Min. Residues	0.010	0.017	0.031	0.112	0.014	0.020	0.010	0.011	0.143	0.010
Max. Residues	0.191	0.151	0.291	1.870	0.134	0.092	0.121	0.199	2.976	11.837
WHO (2010)	0.02	0.03	0.01	0.01	0.02	0.03	0.01	0.03	0.05	

NOTE: Mean ±SD of triplicate, ND = Not Detected

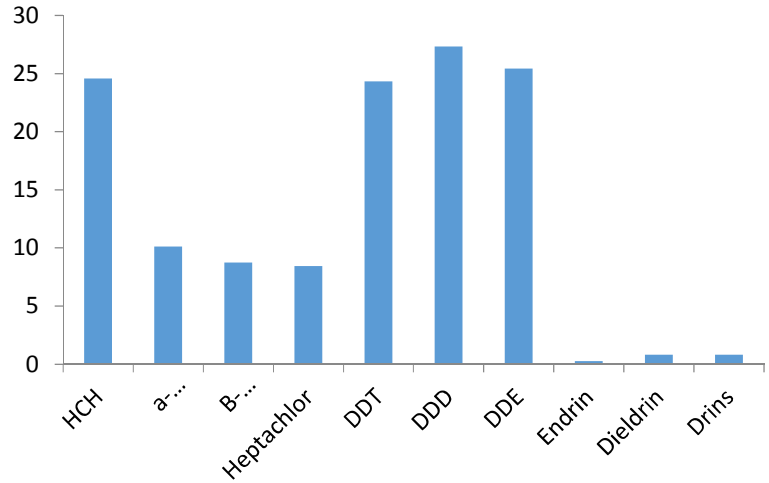

Fig. 2: Percentage distribution of organochlorine residues in the samples

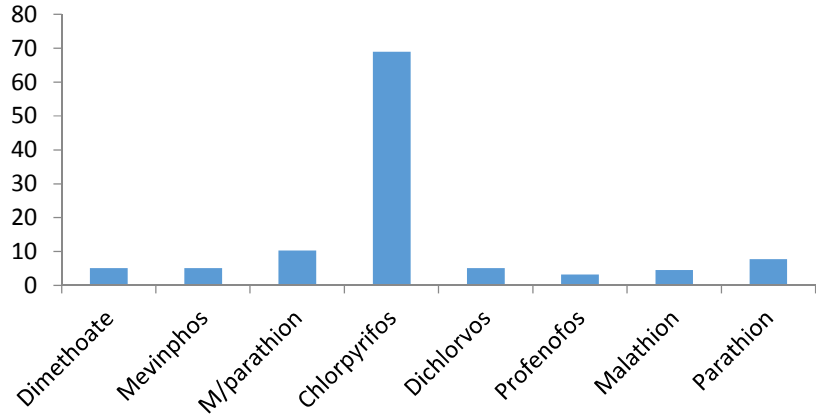

Fig. 3: Percentage distribution of organophosphorus residues in the samples

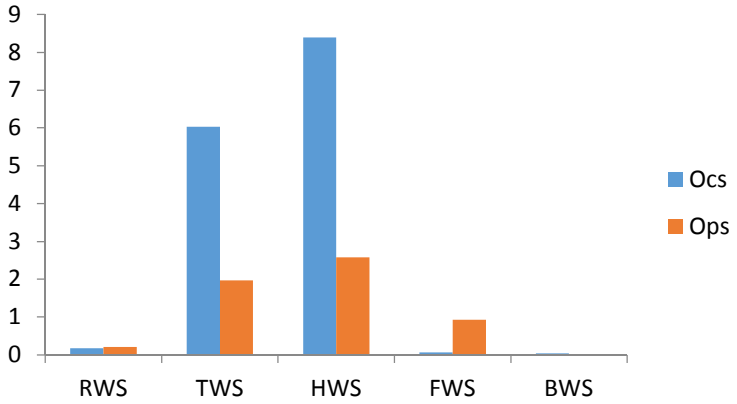

Fig. 4: Comparison between organochlorine and organophosphorus residues in the samples

Discussion

The results of this study indicated the presence of organochlorine (OC) and organophosphorus (OP) pesticide residues in the water samples collected from Wurno irrigation farm and environs.

Organochlorines

γ-HCH: Among the organochlorines in table 1 γ-HCH was detected in 18 samples with a mean concentration of 0.896µg/L and a percentage distribution of 24.5% making it the third most detectable residue in the samples. This value is however higher than the maximum allowable limit set by WHO. Hexachlorocyclohexane (HCH) is used against sucking and biting pest and as smoke for control of pests in grain sores. HCH, previously called BHC (benzene hexachloride), is a mixture of eight isomers of which five are found in the crude product (α, β, γ, δ, ε). Only the γ-isomer or lindane has powerful insecticidal properties. It is very effective against a wide variety of insects, including domestic insects and mosquitoes. γ-HCH (lindane) appears in the list of pesticides for restricted use. Only γ-isomer of HCH was detected in the water samples analysed, which might be because γ-HCH is more resistant to biological and chemical degradation under aerobic conditions (El beit *et al*, 1981) and is most commonly used.

α-endosulfan a broad-spectrum insecticide and acaricide pesticide was detected in 13 samples with a mean concentration of 0.367µg/L having a percentage distribution of 10.0%. The maximum residue concentration of 0.910µg/L detected in HWS1 sample is higher than the maximum limit set by WHO.

β-endosulfan another isomer of endosulfan was detected in 14 samples with a mean concentration of 0.316µg/L having a percentage distribution of 8.63%. Both isomers of endosulfan have potent insecticidal effects, and their presence in this matrix shows both past and present usage.

Heptachlor was detected in 15 samples with a mean concentration of 0.313µg/L having a percentage distribution of 8.55%. Heptachlor (banned with effect from September 20, 1996), with individual maximum limit of 0.770µg/L in HWS2 sample is higher than the maximum limit set by WHO.

DDT was detected in 16 samples with a mean concentration of 0.894µg/L having a percentage distribution of 24.4% of the detectable residues. DDT was detected in most of the samples perhaps due to its persistent nature. Since DDT is known to undergo

metabolic conversion and dehydrochlorination, presence of metabolites of DDT i.e DDD and DDE encountered in this study might be due to such metabolic processes.

DDD with a mean concentration of 1.002µg/L. and a percentage distribution of 27.32% has the highest level of residues detected. The second most detectable residue found in the samples was DDE with a mean concentration of 0.927µg/L. The existence of DDT along with its metabolite, DDD and DDE is an indication of both past and present usage.

The low level of residues detected in endrin with a mean concentration of 0.015µg/L, dieldrin 0.026µg/L and drins 0.08µg/L, could be attributed to their low usage in the study area.

The higher value of 1.002µg/L realized for DDD in Table 1 indicated that there is a higher concentration of the metabolites of DDT in the water although DDT itself may be lower in concentration in this particular field. The persistence of these metabolites may find their residence in the soil sediments as is peculiar in most water bodies. The pesticides may also be drifted by air current or introduced into the water body as a result of run offs.

Organophosphorus:
Among the organophosphorus residues reported in table 2, dimethoate was detected in 13 samples with a mean concentration of 0.080µg/L and has a percentage distribution of 5.12% of the total detectable residues. The individual maximum residue limit of 0.191µg/L is many times higher than the maximum permissible limit set by WHO. Dimethoate is a systemic and contact insecticide and acaricide, effective against red spider mites and thrips on most agricultural and horticultural crops.

Mevinphos was detected in 11 samples with a mean concentration of 0.086µg/L and has a percentage distribution of 5.50%. The existence of this pesticide in the sample could be attributed to its usage in the catchment as a contact insecticide, and has been often found in water samples due to its high solubility.

Methylparathion was detected in 15 samples with a mean value of 0.162µg/L, having a percentage distribution of 10.3%. the maximum level of 0.291µg/L observed in HWS4 sample is many times higher than the maximum allowable limit.

Chlorpyriphos with a mean concentration of 1.073µg/L has the highest level of detectable organophosphorus residues. It has a percentage distribution of 69.03% of the detectable

residues. The high level of chlorpyriphos (an organophosphate pesticide) with a percentage distribution of 69.03% (Fig.3) observed in this work could be attributed to high initial usage and frequency of application as this substance forms a major component of several pesticide formulations.

Profenofos, malathion and dichlorvos with mean concentration of 0.048µg/L, 0.068µg/L and 0.085µg/L respectively are the lowest organophosphorus residues detected.

Malathion and parathion are an important and widely used contact insecticides and acaricides for the control of aphids, red spider mites, leaf hoppers and thrips on a wide range of vegetable and other crops. They are also used to control insect vectors like mosquitoes, and are rapidly absorbed by practically all routes including the gastrointestinal tract, skin, mucous membranes, and lungs. Malathion requires conversion to malaoxon to become an active anticholinesterase agent.

Comparing the residues distribution in the sample revealed that the OCs generally have higher values than the OPs. HWS samples have the highest concentration with a mean value of 8.395µg/L (Fig. 4). And TWS with a concentration of 6.034µg/L was the next abundant residues detected. The high level of residues observed in these samples is directly connected to farming activities in the sampled area. Hand dug wells of which the HWS samples were taken are located directly in the field where the pesticides are applied. Again all the farm implement used in farming activities including the spray, containers used in pesticide formulations are washed therein.

The OPs have higher concentration than the OCs in RWS 0.216µg/L compare to 0.187µg/L of the OCs. The concentration of 0.216µg/L observed in OPs of RWS was higher than the 0.18µg/L observed in the OCs. This could be related to the fact that the OPs are more soluble in fresh water bodies than the OCs pesticide residues.

The organophosphorus pesticides are less persistent in water, soil, food and feed for animals than the organochlorine pesticides; however they are relatively soluble in water and are highly toxic. They break down into nontoxic metabolites. There are a few reports on the concentration of organophosphorus insecticide residues in different rivers of the world (Agarwal, 1997) and drinking water (Mukherjee *et al.*, 1980; Raju *et al.*, 1982). Few organophosphates have been detected in surface water or groundwater (Bansal and Gupta, 2000; Ray, 1992).

The results also revealed that none of the OPs residues was detected in the bored-hole (ground water) samples. The OPs have very low leaching potentials and are seldom found in ground water system (Ray, 1992).

Generally, higher concentrations are realized for the OCs than the OPs with respect to each water sample as shown in Tables 1 and 2. This is because OC pesticides such as DDT (and its metabolites DDE and DDD) and γ-HCH are resistant to microbial and photolytic degradation, and are therefore persistent in the environment (soils and water) where they are applied, while the OPs are readily deactivated and degraded by microbial activities.

Substantial residue levels of organochlorine insecticides including γ-HCH, DDT, and endrin in water and sediment could indicate possible illegal usage in the study area (Wandiga, 2001) and/or their persistence from previous application before they were banned in 1997. The metabolite dieldrin (0.026µg/L) was approximately thrice the concentration of its parent compound endrin (0.015µg/L) in the sample. Dieldrin is also a pesticide on its right but it was not, however, known whether endrin or dieldrin had been applied in the study area. Higher concentrations of the pesticide residues (except α-endosulfan, β-endosulfan and heptachlor) were detected in tube well and hand dug well samples compared with those detected in the river and fresh water samples and this is in agreement with studies of organochlorine pesticide residues in water and sediment samples, which have shown that the concentrations of organochlorine pesticide residues in tube wells are generally higher than their corresponding concentrations in the river water (Crawford, 2004).

In general, the concentrations of the residues in water in this study were higher than the WHO drinking water limits of 0.01µg/L for individual pesticide and 1.0µg/L for total pesticide concentration and similar levels reported in other agricultural sub-catchment sites in other tropical ecosystems such as in a banana plantation system in Jamaica (USEPA, 2002; Mansingh and Wilson, 2005), showed that the water samples collected from this site was contaminated with various pesticide residues, including dieldrin, DDT, HCH, endrin, alachlor, diuron, and endosulfan during the sampling period.

A comparison of the residue concentrations obtained in this study with those of other contaminated environments in other regions such as Kingston Harbourb (Mansingh and Wilson, 2005) shows that this Wurno irrigation farm was relatively more contaminated with residues of pesticides such as dieldrin, endosulfan, and DDT with water concentrations being about four, ten, and twenty times higher, respectively. Alpha BHC, beta-BHC, heptachlor epoxide, aldrin, DDT, and DDE with residue levels of 1.38, 2.33,

1.39, 2.72, 1.39, and 1.15µg/g, respectively, have been detected at comparatively high levels in water samples from a freshwater system in Turkey (Barlas, 2002).

The high concentrations of pesticide detected in water samples from Lugu river mplied a potential threat to the ecology of this sub-catchment as has been reported in other studies (Kreuger, 1998; Ewald and Aebisher 2000; Bach *et al*. 2001; Miiller *et al.* 2002; SETAC, 2003; De Snoo and van der Poll, 1999; Schulz and Liess, 1999; Berenzen *et al*. 2005).

Similarly, Odamah *et al.,* (2009), studying the effect of pesticides used in cocoa plantation in Idoani, Ondo state, Nigeria, on human health however recorded lower concentration of OCs, such as DDT 0.003µg/L, HCH 0.002µg/L, endosulfan 0.001µg/L, endrin 0.001µg/L. The low level of residues recorded in this study could be attributed to low usage of these pesticides in cocoa plantation compared to the intensive usage in Wurno irrigation farm.

Also the concentrations of chlorinated pesticide residues obtained in this study were higher when compared to the residues obtained by Ize-Iyamu *et al.* (2007) in their studies of Ovia, Ogba and Ikoro Rivers in Edo State, Nigeria. The mean pesticide residues obtained were higher than 0.0008µg/L DDT, 0.0004µg/L endosulfan and 0.0001µg/L endrin obtained by Tongo, (1985) from studies carried out in some rivers in Nigeria.

In Nigeria, Federal Environmental Protection Agency FEPA (1991), has established criteria, guidelines, specifications and standards for pesticides usage. FEPA standard for maximum allowable limits for water is 0.1 mg/L. The results from this study show that many of the samples especially the OCs exceeded this limit indicating a scope of environmental contamination and the extent of pollution of the environment.

Conclusion

The pesticide residue analysis of the water samples from Wurno agricultural farm recorded varying values indicating the presence of organochlorine (OC) and organophosphorous (OP) pesticides residues in the water bodies.

Among the OCs analysed, DDD which is a metabolite of DDT was in a higher concentration followed by DDE and then γ-HCH. Among the OPs analysed, Chlorpyrifos was in a higher concentration followed by methylparathion both of which are widely used as agricultural insecticides and also has many uses in households for pest control.

Although the total pesticide residue levels in the individual water from Fresh water samples and Borehole water each is less than 4 µg/L (Tables 1 and 2) and considered by Biney, (2002) as unpolluted, the values obtained for pesticides residues especially for other samples (HWS and TWS) are high enough to pose a risk to the health of organisms, mammal and humans who obtain their nutrition from them. The problems posed by these pesticides become an issue as they may bio-accumulate in the bodies of aquatic organisms that dwell in them and the effect of these pesticides magnifies higher up the food chain.

Although only a small percentage of the bored-hole water were found to have pesticides residues and the concentrations found below levels of concern, these findings do indicate that pesticides can potentially contaminate the groundwater used by home owners.

The concentration levels of individual pesticide residues including γ-HCH, DDT,and its metabolites (DDD, DDE), heptachlor, chlorpyriphos, methylparathion, detected in samples exceeded the WHO drinking water limit requirement of 0.5 µg/L (WHO., 2010). This indicates potential health risks to the local community who depend on the water for drinking and other domestic needs.

The Federal Environmental Protection Agency had published regulations on the control of various types of pesticides within the Nigerian environment. Therefore, there is need to monitor and enforce the existing laws on the production, transportation and use of banned pesticides as stipulated by the Federal Ministry of Environment in Nigeria.

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